# Formation of $[Mn(\eta\text{-}C_5H_5)O_2]$ by Photooxidation of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ in Low-temperature Matrices containing $O_2$

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The UV/VIS irradiation of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ in low-temperature matrices containing 25% $O_2$ led to the formation of a product **A** which, alongside absorptions assigned to a co-ordinated cyclopentadienyl ring, shows features in the IR spectrum at 938.0 and 893.0 $cm^{-1}$. On the basis of experiments involving isotopic substitution with $^{18}O$ these bands are assigned respectively to $\nu_{asym}$ and $\nu_{sym}$(O–Mn–O) vibrations of an $MnO_2$ unit. Species **A** is thus identified as the hitherto unknown organometallic oxide $[Mn(\eta\text{-}C_5H_5)O_2]$ where the manganese atom is formally in the unusual +V oxidation state. The $^{16}O$–$^{18}O$ isotopic shift of $\nu_{asym}(MnO_2)$ of **A** gives an upper limit of 120 ± 8° for its O–Mn–O bond angle (θ). The intensity ratio of the bands arising from $\nu_{sym}$ and $\nu_{asym}(MnO_2)$ suggests a value of 110 ± 5° for the same angle.

Organometallic oxides of rhenium, *e.g.* $ReMeO_3$[1] and $[Re(C_5Me_5)O_3]$,[2] are well characterized compounds which have been implicated as useful catalysts for a range of important chemical processes including olefin oxidation, metathesis and polymerization.[3–6] Not surprisingly, analogous organometallic oxides of manganese are unknown since manganese in high oxidation states is a potent oxidizer of organic groups. One aim of our current research is to use matrix isolation to stabilize organometallic oxides, including those of manganese, which are unstable under normal conditions. We anticipated that a convenient route to such oxides would be *via* photooxidation of metal carbonyl derivatives: such a process is well established as a means of generating *molecular* matrix-isolated metal oxides from binary metal carbonyls[7–9] and has recently been used to form the oxochlorides $MnO_nCl \cdots CO$ ($n = 2$ or 3) and $ReO_3Cl$ from $[MnCl(CO)_5]$ and $[ReCl(CO)_5]$ respectively.[10] In this paper we report results which show that the manganese carbonyl derivative $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ is oxidized under these conditions to yield the oxide $[Mn(\eta\text{-}C_5H_5)O_2]$, where the manganese atom is in the unusual oxidation state of +V.

## Experimental

The matrix-isolation apparatus used at Reading has been described in detail elsewhere.[9] The sample of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (Ethyl Chemical Co.) was recrystallized from hexane prior to use and held at 0 °C for deposition with $O_2$–Ar mixtures by slow spray on. The matrix support was a CsI window cooled to *ca.* 20 K using an Air Products Displex closed-cycle refrigerator. The IR spectra were recorded using a Perkin Elmer model 983 spectrometer which gave a typical resolution and accuracy not exceeding 0.5 $cm^{-1}$. The matrix gases Ar (stated purity 99.998%) and $^{16}O_2$ (stated purity >99.6%) were used as supplied by Aldrich. Samples of $^{18}O_2$ (isotopic purity 98%) and of 'scrambled' $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ (containing 55 atom % of the isotope $^{18}O$) were used as supplied by Merck, Sharp and Dohme. A 150 W high-pressure xenon lamp (Applied Photophysics) was used as the photolysis source.

## Results and Discussion

Following deposition of the sample, bands arising from the $a_1$ and e ν(CO) modes of matrix-isolated $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ can clearly be seen at 2031.5 and 1949.0 $cm^{-1}$ respectively.[11] Weaker bands are also seen in the region 600–1500 $cm^{-1}$ which may be assigned to δ(Mn–C–O) modes (670.0 and 642.0 $cm^{-1}$) or to motions of the cyclopentadienyl ring (1425.0, 1116.0, 1015.0/1010.0, 846.0 and 831.5 $cm^{-1}$).[12] Upon photolysis all of these bands decline in intensity; after *ca.* 5 h of photolysis the IR spectra show that the starting compound has disappeared and that there are no other metal carbonyl species present within the matrix. At the same time bands due to matrix-isolated free CO[13] and $CO_2$[14] appear and grow. Further bands develop at positions as listed in Table 1. All of these features grow at a constant rate (Fig. 1) and thus may be assigned to a single species **A**. The relative intensities of these features was unaffected by altering the composition of the matrix or by changing the photolysis wavelength even though the overall rate of reaction was changed by such procedures. Those bands designated by the symbol * in Table 1 and in Fig. 1 are in the correct region of the spectrum to arise from a co-ordinated cyclopentadienyl group.[12]

Unfortunately 'free' cyclopentadienyl, $C_5H_5$, has only been detected in low-temperature matrices by means of its ESR spectrum.[15] Thus it is not possible to be completely certain, on the basis of our IR spectra, that there is no 'free' cyclopentadienyl present within the matrix at this stage of photolysis. Although the matrix photooxidation of cyclopentadienyl has not been studied it is known that the carbene $C_5H_4$ is readily oxidized photochemically in low-temperature matrices[16] and also that cyclopentadiene is itself easily oxidized in solution.[17] The products of these reactions include molecules containing O–H, C=O and C–O–C groups. There is no sign of any such product in any of our experiments described in this paper,[18] and it seems unlikely that cyclopentadienyl would be inert to

**Table 1** Observed IR bands assigned to $[Mn(\eta^5\text{-}C_5H_5)O_2]$ A; those marked * arise from vibrations of the cyclopentadienyl ring

| $\tilde{\nu}/cm^{-1}$ | Approximate description |
|---|---|
| 1421.0 | ν(C–C)* |
| 1020.0 | ν(C–C)* |
| 1006.0 | δ(C–H)* |
| 938.0 | $\nu_{asym}(MnO_2)$ |
| 893.0 | $\nu_{sym}(MnO_2)$ |
| 820.5 | π(C–H)* |
| 793.5 | π(C–H)* |

**Table 2** Behaviour of bands assigned to ν(Mn=O) vibrations of species **A** upon $^{18}O$ substitution

| $\tilde{\nu}(^{16}O_2)/cm^{-1}$ | $\tilde{\nu}(^{16}O^{18}O)/cm^{-1}$ | $\tilde{\nu}(^{18}O_2)/cm^{-1}$ | $\Delta\tilde{\nu}^a/cm^{-1}$ | $R^b$ | $\rho^c$ |
|---|---|---|---|---|---|
| 938.0 | 923.0 | 901.0 | 37.0 | 0.9606 | 0.811 |
| 893.0 | 870.0 | 858.5 | 34.5 | 0.9614 | 1.333 |

[a] $\Delta\nu = \nu(^{16}O_2) - \nu(^{18}O_2)$. [b] $R = \nu(^{18}O_2)/\nu(^{16}O_2)$. [c] $\rho = 2[\nu(^{16}O_2) - \nu(^{16}O^{18}O)]/[\nu(^{16}O_2) - \nu(^{18}O_2)]$.

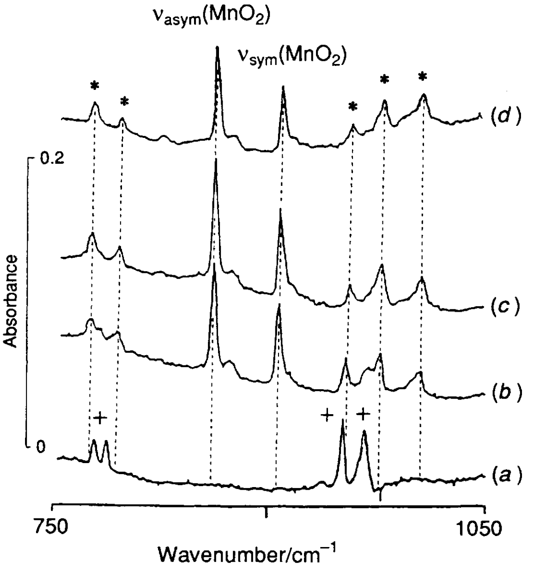

**Fig. 1** The region 750–1050 cm$^{-1}$ of the IR absorption spectrum of a matrix initially composed of $[Mn(\eta^5-C_5H_5)(CO)_3]$, $O_2$ and Ar in the approximate proportions 1:250:1000; (*a*) after deposition at 20 K, (*b*) after 30 min of broad-band UV/VIS irradiation, (*c*) after 120 min of such irradiation, and (*d*) after 260 min of such irradiation. Bands marked + arise from vibrations of the cyclopentadienyl ring of the starting material, while those marked * arise from vibrations of the cyclopentadienyl ring of **A**

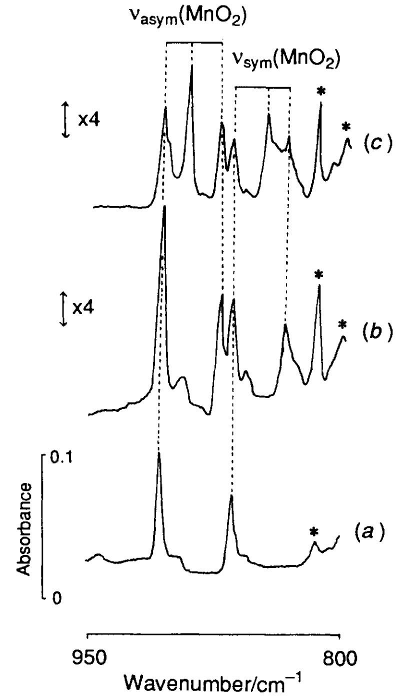

**Fig. 2** The region 800–950 cm$^{-1}$ of the IR absorption spectrum of $O_2$-doped argon matrices initially containing *ca.* 0.1% $[Mn(\eta^5-C_5H_5)(CO)_3]$ after 260 min of broad-band UV/VIS irradiation. Matrix composition: (*a*) $^{16}O_2$:Ar = 25:100; (*b*) $^{16}O_2$:$^{18}O_2$:Ar = 13.75:11.25:100; (*c*) $^{16}O_2$:$^{16}O^{18}O$:$^{18}O_2$:Ar = 7.5:12.5:5.0:100. Bands marked * arise from vibrations of the cyclopentadienyl ring of species **A**. The absorbance scale of spectra (*b*) and (*c*) has been expanded by a factor of four when compared with that of (*a*)

oxidation under the conditions. These findings provide further *circumstantial* evidence that the cyclopentadienyl groups remain bound to the manganese centre during photolysis, so it would seem reasonable to propose that **A** contains a cyclopentadienyl group. It is, of course, not possible to tell from IR spectroscopy alone whether this group shows $\eta^5$ or some other form of ligation.[12] The remaining bands of **A** at 938.0 and 893.0 cm$^{-1}$ are in the correct region of the spectrum to arise from ν(Mn=O) vibrations.[9,10,12]

In order to confirm these assignments and to attempt an identification of **A** we carried out experiments using the isotope $^{18}O$. When $^{16}O_2$ is replaced by a mixture (55:45) of $^{16}O_2$ and $^{18}O_2$ and the experiment is repeated the bands at 938.0 and 893.0 cm$^{-1}$ each give way to a pair of doublets [Fig. 2(*b*)]. The observation of *a pair of doublets* is only compatible with **A** containing a dioxomanganese unit where both O atoms have been derived from the same $O_2$ molecule. A monoxomanganese species would give just one doublet [since it would necessarily show only one ν(Mn–O) vibration]. The $^{16}O$–$^{18}O$ shifts for these bands (938.0, shift = 37.0; 893.0, shift = 34.5 cm$^{-1}$) are entirely compatible with an assignment of the bands to $\nu_{asym}$ and $\nu_{sym}(MnO_2)$ respectively.[9,10] They are too small to allow an assignment of either band to ν(O–O) of a co-ordinated $O_2$ unit (expected shifts: 938.0, shift = 54.0; 893.0, shift = 52.0 cm$^{-1}$) or to ν(Mn=O) of an MnO (monoxo) unit (expected shifts: 938.0, shift = 41.0; 893.0, shift = 39.0 cm$^{-1}$).

We then repeated the experiment using a 'scrambled' mixture of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$. It can be seen [Fig. 2(*c*)] that the pair of doublets seen above have each given way to a pair of *unsymmetrical* triplets (see Table 2 for wavenumber values). The asymmetry parameters[7] for these triplets (0.811 and 1.33 respectively) are entirely in order for $\nu_{asym}$ and $\nu_{sym}(MnO_2)$ vibrations where $\nu_{asym} > \nu_{sym}$ and where the two fundamentals are separated by only 48 cm$^{-1}$ and thus couple quite strongly for the mixed $^{16}O^{18}O$ isotopomers. As expected the bands assigned to modes of the co-ordinated cyclopentadienyl ring do not shift upon $^{18}O$ substitution. The behaviour of the observed bands upon $^{18}O$ substitution is listed in Table 2.

These spectra are incompatible with a molecule containing an $MnO_3$ unit. In this case both experiments with a mixture of $^{16}O_2$ and $^{18}O_2$ and with 'scrambled' $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ would be expected to give rise to a pair of *quartets* of bands[7c,8b] arising from the various isotopomers of the $MnO_3$ unit when substituted by $^{18}O$.

We have thus obtained a body of spectroscopic evidence which shows that species **A** contains a co-ordinated cyclopentadienyl ring and an $MnO_2$ unit, *i.e.* $Mn(\eta-C_5H_5)O_2$. It is possible to estimate the O–Mn–O bond angle of **A** (θ) by: (*i*) measurement of the relative intensity of the bands arising from $\nu_{asym}$ and $\nu_{sym}(MnO_2)$[7,19] and (*ii*) by measuring the $^{16}O$–$^{18}O$ isotopic shift of $\nu_{asym}(MnO_2)$.[7,20,21] The former method gives a value of θ = 110 ± 5° for the measured intensity ratio of $\nu_{asym}:\nu_{sym}$ = 2.4:1. The latter method gives an *upper limit* for θ of 120 ± 8°. Thus the two values are consistent and suggest an O–Mn–O bond angle in the range 110–120°.

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## References

1 I. R. Beattie and P. J. Jones, *Inorg. Chem.*, 1979, **18**, 2318.

2 W. A. Herrmann, M. Taillefer, C. de M. de Bellefon and J. Behm, *Inorg. Chem.*, 1991, **30**, 3247; W. A. Herrmann, *J. Organomet. Chem.*, 1990, **382**, 1.

3 W. A. Herrmann, R. W. Fischer and D. W. Marz, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1636.

4 W. A. Herrmann and M. Wang, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1641.

5 V. Drugaten, A. T. Baladen and M. Dimonie, *Olefin Metathesis and Ring Polymerisation*, Wiley, New York, 1985.

6 T. Kawai, M. Goto, T. Ishikawa and Y. Yamasaki, *J. Mol. Catal.*, 1987, **39**, 369.

7 (*a*) J. A. Crayston, M. J. Almond, A. J. Downs, M. Poliakoff and J. J. Turner, *Inorg. Chem.*, 1984, **23**, 3051; (*b*) M. J. Almond, J. A. Crayston, A. J. Downs, M. Poliakoff and J. J. Turner, *Inorg. Chem.*, 1986, **25**, 19; (*c*) M. J. Almond and A. J. Downs, *J. Chem. Soc., Dalton Trans.*, 1988, 809; (*d*) M. J. Almond and M. Hahne, *J. Chem. Soc., Dalton Trans.*, 1988, 2255.

8 (*a*) M. Fanfarillo, H. E. Cribb, A. J. Downs, T. M. Greene and M. J. Almond, *Inorg. Chem.*, 1992, **31**, 2961; (*b*) M. Fanfarillo, A. J. Downs, T. M. Greene and M. J. Almond, *Inorg. Chem.*, 1992, **31**, 2973.

9 M. J. Almond, *J. Mol. Struct.*, 1988, **172**, 157; M. J. Almond and R. H. Orrin, *J. Chem. Soc., Dalton Trans.*, 1992, 1229.

10 M. J. Almond and R. H. Orrin, *Polyhedron*, 1992, **11**, 2157.

11 A. J. Rest, J. R. Sodeau and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1978, 651; N. J. Fitzpatrick, A. J. Rest and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1979, 351; M. Heberhold, W. Kremnitz, H. Trampisch, R. B. Hitam, A. J. Rest and D. J. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 1261.

12 K. Nakamoto, *Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

13 H. Dubost, *Chem. Phys.*, 1976, **12**, 139.

14 L. Fredin, B. Nelander and G. Ribbegard, *J. Mol. Spectrosc.*, 1974, **53**, 10.

15 P. H. Kasai and D. McLeod, jun., *J. Am. Chem. Soc.*, 1974, **96**, 2338.

16 O. L. Chapman and T. C. Hess, *J. Org. Chem.*, 1979, **44**, 962; I. R. Dunkin and C. J. Shields, *J. Chem. Soc., Chem. Commun.*, 1986, 154; G. A. Bell, I. R. Dunkin and C. J. Shields, *Spectrochim. Acta, Part A*, 1985, **41**, 1221; G. A. Bell and I. R. Dunkin, *J. Chem. Soc., Chem. Commun.*, 1983, 1213; O. L. Chapman and T. C. Hess, *J. Am. Chem. Soc.*, 1984, **106**, 1842.

17 K. A. Saegebarth, *J. Org. Chem.*, 1960, **25**, 2212; M. Korach, D. R. Nielson and W. H. Rideout, *J. Am. Chem. Soc.*, 1960, **82**, 4328.

18 W. Kemp, *Organic Spectroscopy*, 2nd edn., Macmillan, Basingstoke, 1987.

19 E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955; W. Levason, R. Narayanaswamy, J. S. Ogden, A. J. Rest and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1992, 2009.

20 D. W. Green, D. W. McDermott and A. Bergman, *J. Mol. Spectrosc.*, 1983, **98**, 111.

21 M. Poliakoff, K. P. Smith, J. J. Turner and A. J. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1982, 651.

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